

SOME CHARACTERISTICS OF PHASE FORMATION IN COMBUSTION OF POWDERED TITANIUM-SILICON AND MOLYBDENUM-SILICON MIXTURES

A. R. Sarkisyan, M. M. Sarkisyan, and S. L. Kharatyan

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The phase formation processes in Ti-Si and Mo-Si systems were studied, using special markers simulating the behavior of large metal particles after they have passed the combustion front. It is shown that, depending on the combustion temperatures of the mixtures, phases can be formed by joint crystallization from the eutectic melt, or disilicides crystallize first and intermediate phases (Mo_5Si_3 and $TiSi$) form by a solid-phase mechanism.

In recent years, combustion processes in Me-Si systems and SHS synthesis of silicides of transition metals have been dealt with in several studies [1-6]. Their authors have shown that the melting of silicon in the heating zone and the presence of a liquid phase in the interaction process are of decisive importance in the metal powder-silicon interaction. It should be noted that after the liquid phase (the eutectic melt) disappears, the chemical interaction stops almost completely. It has also been shown that Me-Si systems are weakly eutectic and highly sensitive to heat losses: with slight heat losses, intermediate phases are observed, along with incomplete combustion.

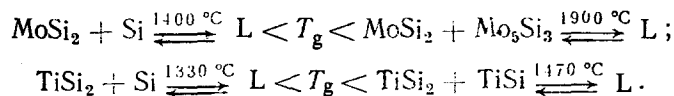
This study was carried out to investigate phase-formation processes in the combustion of binary mixtures of titanium-silicon and molybdenum-silicon powders. It is known that phase-formation processes occur mainly in the after-burning region and that their characteristic features are exhibited most distinctly in large metal particles. Therefore, special markers (titanium and molybdenum wires covered with a solid layer of silicon and placed in the charge), simulating the behavior of large metal particles after passing the combustion front, were used in the studies.

The experiments were carried out in molds with quartz sand as a medium on pellets with $d = 15$ to 50 mm, $h = 10$ to 30 mm, and the relative density $\Delta = 0.4$ to 0.7 . Silicon with dispersity of less than $40 \mu\text{m}$, molybdenum powder with a particle size of 3 to $10 \mu\text{m}$, and titanium powder with a particle size of less than $50 \mu\text{m}$ were used as initial materials. The combustion temperature of the mixture the time of occurrence of the eutectic melt in the liquid state (the cooling rate of the specimen) were controlled by varying the ratio of initial reactants, the preheating and dilution of the mixture, the thermal conductivity of the medium of synthesis, etc. (Fig. 1).

Information about the peculiarities of the process was obtained by investigating the silicide layers, produced on the wires. The microstructure of the specimens was examined in a BS-300 electron microscope and a USKhA-733 Superprobe X-ray analyzer. X-ray analysis was performed on a DRON-0.5 diffractometer.

We will consider some typical cases of combustion of powdered Mo-Si and Ti-Si mixtures.

I. The combustion temperatures of the mixtures lie between the temperatures of eutectic equilibria:



One can see in the micrographs of sections of metallographic specimens that on the molybdenum wire (Fig. 2a) $MoSi_2$ and Mo_5Si_3 phases are formed and on the titanium wire $TiSi_2$ and $TiSi$ phases appear. It should be noted that the $TiSi$ phase was only observed in the case of longer existence of the liquid phase (the synthesis was conducted in a medium with thermal conductivity lower than that of quartz sand). The $MoSi_2$ and $TiSi_2$ phases

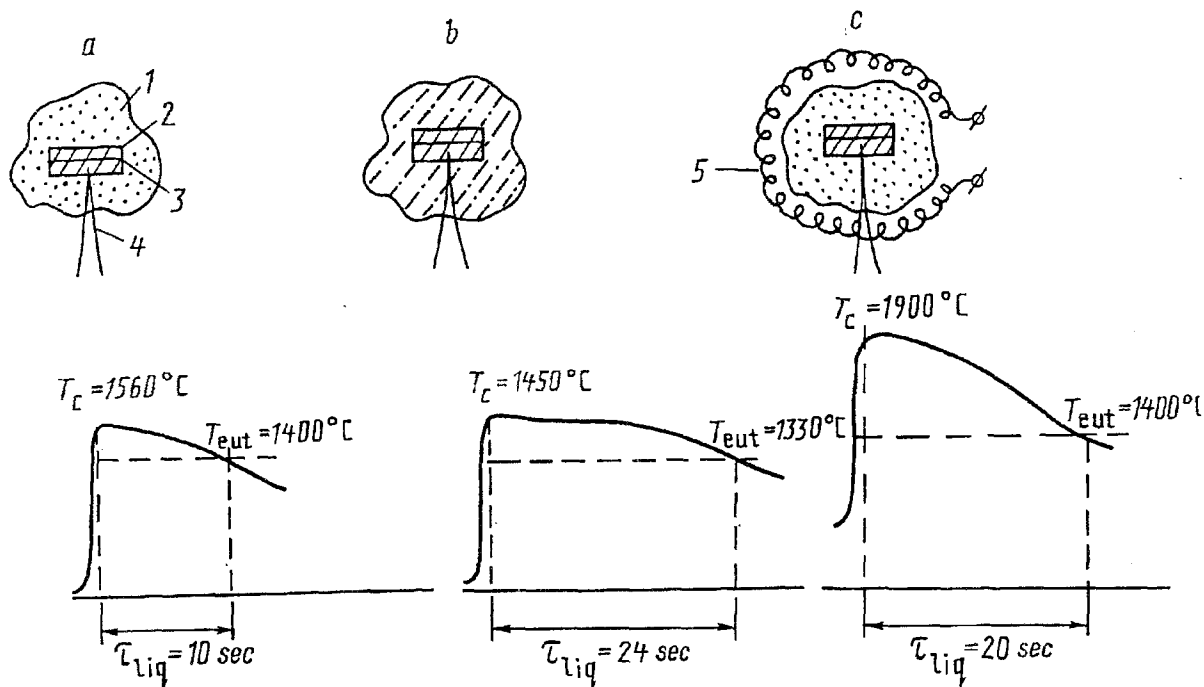


Fig. 1. Typical thermograms in combustion of mixtures of powdered molybdenum (a, c) and titanium (b) with silicon: a) Mo + 1.8Si mixture; b) Ti + 1.9Si mixture; c) Mo + 2Si mixture with the preheating temperature $T_h = 550^\circ\text{C}$; 1) medium of the synthesis; 2) reaction mixture; 3) silicon-coated metal wire; 4) thermocouple; 5) preheating.

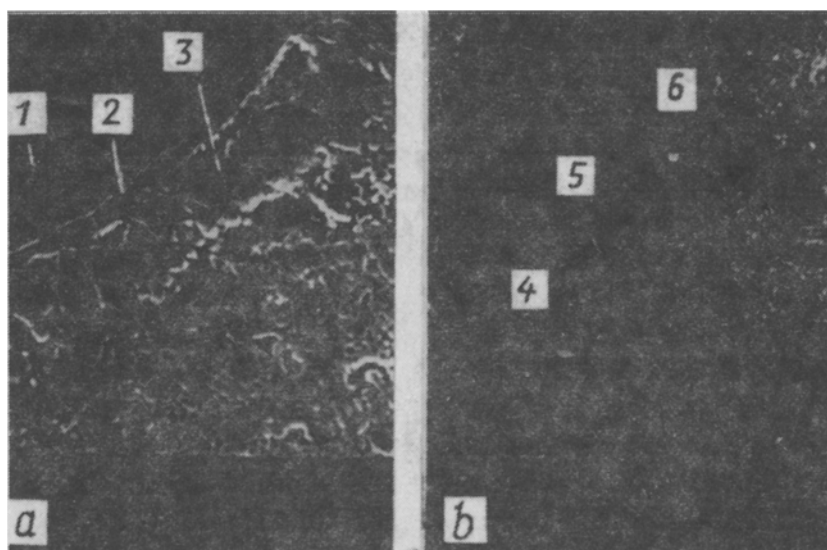


Fig. 2. Micrographs of sections of metallographic specimens of molybdenum (a) and titanium (b) wires: a) $T_c = 1560^\circ\text{C}$; $\tau_{\text{liq}} = 10$ sec; b) $T_c = 1450^\circ\text{C}$; $\tau_{\text{liq}} = 24$ sec; 1) molybdenum wire; 2) Mo_5Si_3 phase; 3) MoSi_2 phase; 4) titanium wire; 5) TiSi phase; 6) TiSi_2 phase.

result from crystallization from eutectic melts, and the formation of the Mo_5Si_3 and TiSi phases follows a solid-phase mechanism (see Fig. 2).

II. The combustion temperatures lie between the melting temperatures of MoSi_2 or TiSi_2 and the eutectic equilibria:

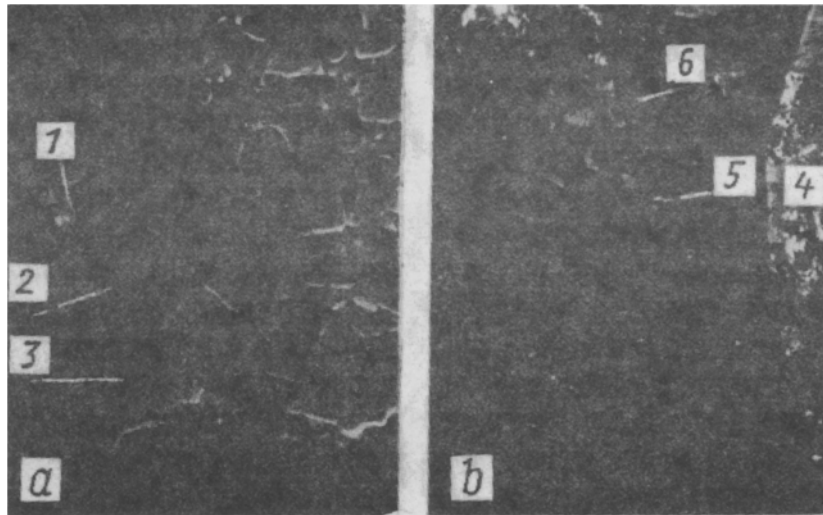
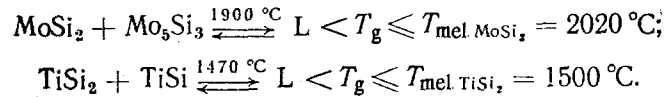


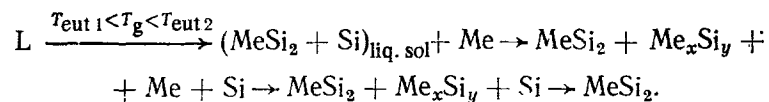
Fig. 3. Micrographs of sections of metallographic specimens of molybdenum (a) and titanium (b) wires: a) $T_c = 1900^\circ\text{C}$; $T_h = 950^\circ\text{C}$; $\tau_{\text{liq}} = 20$ sec; b) $T_c = 1480^\circ\text{C}$; $\tau_{\text{liq}} = 14$ sec. The notation is the same as in Fig. 2.



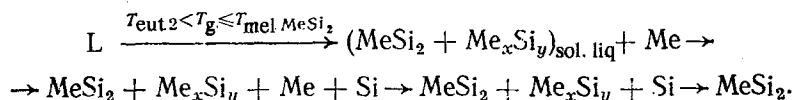
It can be seen from Fig. 3 that the behavior of the phase formation changes. The TiSi_2 , TiSi , and MoSi_2 phases are formed by joint crystallization from the melt.

Thus, the conclusion can be made from the experimental data presented that depending on the combustion temperature, phase formation in the Mo-Si and Ti-Si systems can follow the two mechanisms:

1. In the case of crystallization of the eutectic melt disilicides are produced first. Subsequently, the melt interacts partially with the nonreacted core of a large metal particle to produce the intermediate Me_xSi_y phase. Complete transformation of the cores of large metal particles into disilicide occurs with excessive silicon and minimum heat losses and largely follows the diffusion mechanism through formation of intermediate phases that transform further into disilicide:



2. In the case of crystallization of the melt, disilicide and an intermediate phase crystallize together. Further homogenation and transformation of the nonreacted cores of large metal particles into disilicide also follow the diffusion mechanism (at minimum heat losses and excessive silicon). However, it should be noted that the second case seems preferable in the sense of kinetics, since in this case the main part of the intermediate phase crystallizes from the melt:



NOTATION

d and h , diameter and height of the pellets; Δ , relative density; T_c , combustion temperature; T_{eut} , temperature of the eutectic equilibrium; τ_{liq} , time of occurrence of the melt in the liquid state.

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